BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3017—3018 (1969)

The Cation-exchange Separation of Copper and Iron in Ammoniacal Pyrophosphate Media

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(Received March 31, 1969)

Kharin and Soraka[1] and Marczenko[2] have reported the separation of copper and iron using cation exchange resin in the ammonium form, with sodium pyrophosphate as the eluting agent. In their method, however, much sodium pyrophosphate seems to prevent an ion exchange of copper because sodium ions also exchange with ammonium ions. However, their method merits further study.

The purposes of the present study are to establish a cation-exchange method for the separation of copper from iron using ammonium pyrophosphate instead of sodium pyrophosphate, and to apply it to the determination of copper in hot spring waters. This method is based on the difference in stability[3] between copper and iron pyrophosphate complexes. The separation of copper and iron with cation-exchange resin is affected by the pH and by the concentrations of pyrophosphate and ammonia.

Experimental

Reagent and Apparatus. *Pyrophosphate Solution.* 72 g of pyrophosphoric acid were dissolved in 100 m*l* of distilled water. The solution was adjusted to pH 5 with ammonia and then diluted to 200 m*l*. Copper and other impurities were removed from the solution by extraction with a dithizone carbon tetrachloride solution.

Ammonia Solution. 50 g of ammonium nitrate were dissolved in 50 m*l* of distilled water. Copper and other elements were removed as has been described above. The solution was diluted to 100 m*l* after 36 m*l* of 10 M distilled ammonia had been added. The final solution showed pH 10 and 10 M in ammonia, $NH_3+NH_4^+$.

Washing Solution. This solution was made by mixing 0.5 m*l* of the pyrophosphate and 10 m*l* of the ammonia solution and by then diluting to 100 m*l* with distilled water.

Resin and Column. Dowex 50×8 (50—100 mesh) was converted to the ammonium form with 1 M ammonium chloride. The ion-exchange column was 10 mm in diameter and 100 mm long.

Determination of Copper and Iron. The copper was determined colorimetrically using either cupferazone[4] or dithizone.[5] The iron was determined by the *o*-phenanthroline method.[5] In order to promote color development, solutions were kept at 40°C after adding reagents, and the transmittance was measured at 500 mμ.

Procedure. To a solution containing 50 μg of copper and 500 μg of iron, 0.25 m*l* of the pyrophosphate and 5 m*l* of the ammonia solution were added. The solution was then diluted to 50 m*l* with distilled water and passed through the column at a flow rate of 1.0 to 1.2 m*l*/min. The column was washed with 50 m*l* of the washing solution. The effluent obtained was used to determine the iron. Then, the column was treated

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[1] A. H. Kharin and N. N. Soraka, *Zh. Prikl. Khim.*, **37**, 672 (1964).

[2] Z. Marczenko, *Chemia Analityczma*, **1**, 263 (1956); *Anal. Abstr.*, **4**, Abstract 3569 (1957).

[3] A. Ringbom, "Complexation in Analytical Chemistry," Interscience Publishers, New York (1963).

[4] T. R. Williams and R. R. T. Morgen, *Chem. Ind. (London)*, **1954**, 461.

[5] E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publishers, New York (1959), pp. 453, 537.

TABLE 1. MAJOR COMPONENTS AND COPPER CONTENTS OF THE SAMPLES

Sample	pH	mg/*l*								μg/*l*
		Na	K	Mg	Ca	Al	Fe	Cl	SO_4	Cu
Synthetic solution	0.9	250	200	100	250	800	70	12000	1300	0
Tateyama-jigokudani hot spring*	0.7	244	191	88	248	840	68.6	12340	1314	7
Kankō Hotel spring in Narugo**	2.3	173	15.1	—	—	—	35.3	108	—	5
Karabuki spring in Manza***	1.8	565	105	245	78	56	32.4	966	4170	2

* Analyst: M. Imahashi; ** Analyst: H. Miyazawa; *** Analyst: R. Nakagawa

with 50 m*l* of 2 N hydrochloric acid. This effluent was then used to determine the copper.

Results

The Effect of pH on Separation of Copper and Iron. The pH of the solutions was adjusted to between 8 to 11 with either nitric acid or sodium hydroxide. Iron passed through the column at any pH. The copper was entirely retained in the column at pH 9 to 10, but it was partly lost below pH 9. It was best to separate the copper and iron at pHs from 9 to 10; the recoveries were found to be 99% for copper and 100% for iron.

The Effect of the Concentration of Ammonia, $NH_3+NH_4^+$. The experiments were made on solutions containing up to 2 M of ammonia at pH 9.5. The results showed that the separation of copper and iron was favorable between 1 to 2 M in ammonia, but it was not suitable below 0.5 M because the copper partly passed through the column.

The Effect of the Concentration of Pyrophosphate. The effect of the concentration of pyrophosphate on the separation of copper and iron was examined using sodium, potassium, and ammonium pyrophosphate. The results showed that above 0.05 M sodium and potassium pyrophosphate disturbed the ion exchange of copper because sodium and potassium ions were exchangeable with ammonium ions in the column. On the other hand, ammonium pyrophosphate did not disturb the ion exchange of copper up to 0.5 M in pyrophosphate.

Application

The above method was used in the determination of copper in synthetic samples and hot spring waters. The components of these samples are shown in Table 1.

TABLE 2. DETERMINATION OF COPPER IN SYNTHETIC SOLUTION*

Cu added (μg)	Cu found (μg)
0.0	0.0, 0.0, 0.1
1.0	1.0, 0.9, 0.9
2.0	2.2, 1.9

* Synthetic solution was prepared by dissolving chemical reagent.

A 50-m*l* portion of the sample was placed in a beaker, and then 10 m*l* of the pyrophosphate and 20 m*l* of the ammonia solutions were stirred in.[*1] The solution was diluted to 100 m*l* and passed through the column. The column was washed with 30 m*l* of the washing solution. Then, copper was eluted with 50 m*l* of 2 N hydrochloric acid and determined by the dithizone method.5) The results are shown in Tables 1 and 2. Though traces of copper and a great quantity of iron were found, the error involved in this method was not significant. Moreover, the copper contents in hot spring waters determined by the present method were in good agreement with those reported by Ichikuni.6)

The author wishes to thank Professor K. Noguchi and Dr. M. Ichikuni for their helpful discussions during this work.

[*1] When much aluminum exists in the sample, aluminum hydroxide is gradually formed in the solution. In that case, the precipitate was separated from the solution with a centrifuge and was later dissolved in the elute containing copper.

6) M. Ichikuni, *Geochim. et Cosmochim. Acta*, **23**, 305 (1959).